LA-UR-01-2520
Approved for public release; distribution is unlimited.

Title: **Development of Metallographic Preparation Techniques for Group IVA and VA Elements**

Author(s): Ann M. Kelly, Sherri R. Bingert, Terri G. Abeln, W. Larry Hults, Jason C. Cooley and Dan J. Thoma

Submitted to:

Development of Metallographic Preparation Techniques for Group IVA and VA Elements

Ann M. Kelly, Sherri R. Bingert, Terri G. Abeln, W. Larry Hults, Jason C. Cooley and Dan J. Thoma

Los Alamos National Laboratory, Los Alamos, New Mexico 87545 USA

Existing metallographic preparation techniques for Group IVA/VA (e.g. V, Ti, Ta, Hf, Nb, Zr) materials do not reveal all microstructural features inherent to the process history. As a result, new techniques have been developed and compared to existing procedures. For example, in pure tantalum, the new procedure exposes a substructure that is not evident using previously published techniques. In niobium, better grain boundary delineation is possible with the new process. Similar results are evident for titanium, zirconium, vanadium, and hafnium. The new preparation stage includes a chemical polish and etchant. The chemical polish was found to eliminate problems associated with the mechanical polish. Specifically, the chemical polish removes the worked surface and eliminates smearing. The etching stage serves to delineate the grain boundaries, and in some cases allows bright field as well as polarized or differential interference contrast (DIC) for optical examination. Finally, optical lighting conditions to enhance the observations available with the optimized procedure will be discussed.

Keywords*: metallographic preparation, titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), mechanical polishing, chemical polishing, etching, artifacts, microstructure.*

1. Introduction

A new metallographic preparation has been developed for tantalum and tantalum alloys[1)]. The technique was established primarily to produce grain boundary definition superior to that of typical preparations found in metallographic literature. The preparation procedure consisted of a chemical polish that removed fine residual scratches from the mechanical polishing stage. The new procedure also led to the development of a new etchant which (when used after the chemical polish) produced well- defined grain boundaries without enlarging porosity.

Since the Ta preparation procedure evolved into an efficient metallographic technique, its application to Group IVA and other VA materials was initiated.[2)] Through these studies, it was determined that with only minor adjustments, the process could be extended to other metals with excellent results. This report describes further progress made in the metallographic preparation of Groups IVA and VA metals and compares standard preparation techniques to the new preparation techniques.

2. Specimen Preparation

Samples were mounted under vacuum in a low viscosity epoxy resin. Once fully impregnated, the samples were removed from the vacuum chamber and placed in a pressure vessel to cure at room temperature in a dry nitrogen atmosphere of 600 – 1000 psi for a minimum of 5 hours. The mounting/curing process ensures excellent penetration of the resin to all surface accessible porosity.

After mounting, the samples were wet ground on consecutively finer grit (120 to 1200) SiC grinding papers. To prevent smeared material (a dull gray grease like film) from collecting on the sample surface, grinding paper must be changed frequently and lighter pressure applied during the final (800/1200 grit) grinding stage.

Using the Ta preparation technique,[1,2)] the grinding process was followed by polishing on a low napped cloth using a 3μm diamond suspension and a 25/75 propylene glycol/water extender for approximately 5-6 hours. Specimens were then final polished on a napped cloth using a 1μm suspension and a 25/75 propylene glycol/water extender for approximately 1-2 hours. However, during the rough polishing process it was noted that specimens developed pits and comet tails. These artifacts were attributed to a possible chemical reaction produced by the diamond polishing media or the extender. Subsequent work resulted in an optimized polishing sequence that uses a low-napped cloth with a 0.3μm alumina slurry and a H_2O lubricant for approximately 30 minutes. The coarse polishing on a low napped cloth was followed by final polishing on a napped cloth. Again, 0.3 alumina slurry and a H_2O lubricant were used, but only for approximately 20 minutes. Not only did this sequence eliminate the artifacts, but also reduced the polishing time, and produced a suitable surface for the chemical polish and/or etching phase.

3. Results and Discussion

Metallographic literature suggests the use of a variety of etchants designed for a particular material.[3)] Among the listed etchants, some are extremely hazardous from a safety and environmental standpoint, and therefore considered unsuitable for this study. From the safer list of etchants, the etching process did not always provide robust results. For example, the etchants could yield poorly defined microstructural features, (e.g., lack of low angle grain boundaries), pitted sample surfaces, enhanced inherent porosity and scratched surfaces. However, at least one recommended etchants for the Group IVA and VA metals provided satisfactory results, and the comparative study to the new process is detailed below.

Results of this study are reflected in Figures 1-12, comparing ASTM recommended etchants to the new preparation techniques. For a direct comparison of the etchants, photographs have been placed next to each other in columns. In the left column are samples prepared with the ASTM recommended etchant and in the right column are samples prepared with the new preparation technique. Figures 1 and 2 (heat treated titanium) show very little apparent difference between the two preparation methods (photo in differential interference contrast, DIC). Figures 3 and 4 (zirconium plate stock) indicate very little if any difference in appearance (photo in DIC). Figures 5 and 6

(hafnium plate stock) show a marked improvement with the new preparation, low angle grain boundaries are more

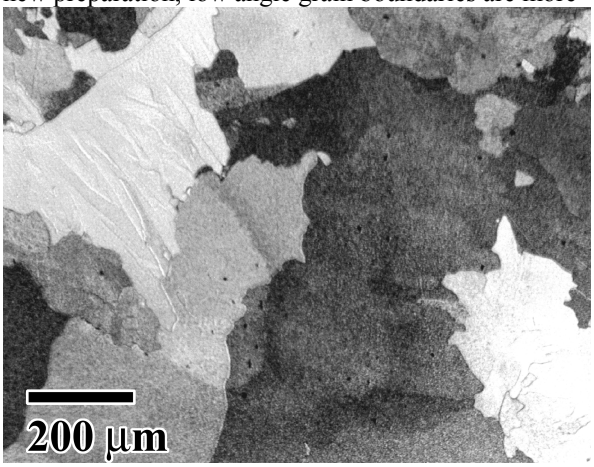

Fig. 1 Heat treated titanium, etchant Krolls (ASTM 192) 100 ml H_2O, 2-6 ml HNO_3, 1-3 ml HF ~ 6 seconds (polarized light or DIC). Photographed in DIC.

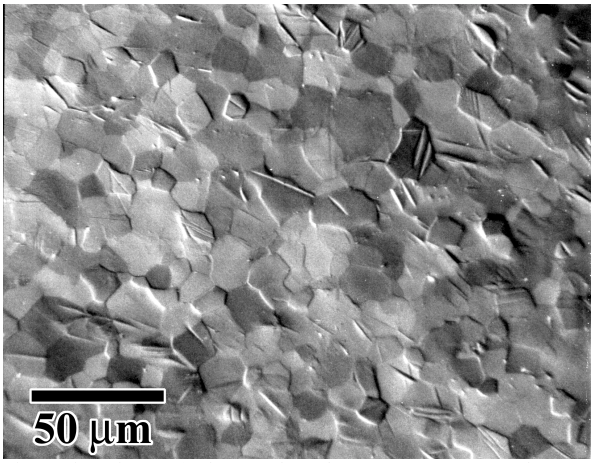

Fig. 3 Zirconium (Zr) plate stock, etchant (ASTM 72). 45 ml H_2O, 45 ml HNO_3, 10 ml HF~ 5-20 seconds (tends to bubble – cycle is complete, when bubbles dissipate). (polarized light or DIC) Photographed in DIC.

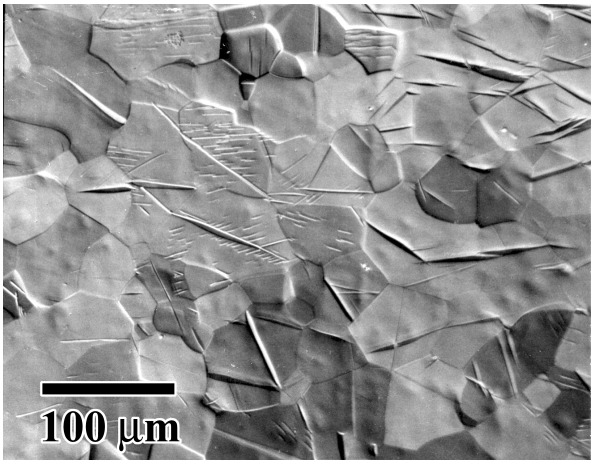

Fig.5 Hafnium (Hf) plate stock. Etchant (ASTM 72) Figure c. 45 ml H_2O, 45 ml HNO_3, 10 ml HF swab for ~ 5 seconds (tends to bubble – cycle is complete, when bubbles dissipate). (polarized or DIC) Photographed in DIC.

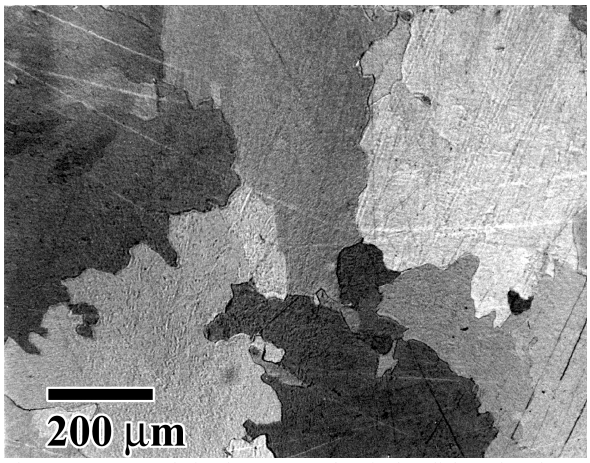

Fig. 2 Heat treated titanium. New chemical polish and etchant, chemical polish 25ml lactic acid, 15 ml HNO_3 ,5 HF for ~ 20 seconds – Etchant 10 ml HNO_3, 10 ml HF, 30ml H_2SO_4 for ~ 30 seconds - grain boundary delineation slightly sharper (polarized light or DIC). Photographed in DIC.

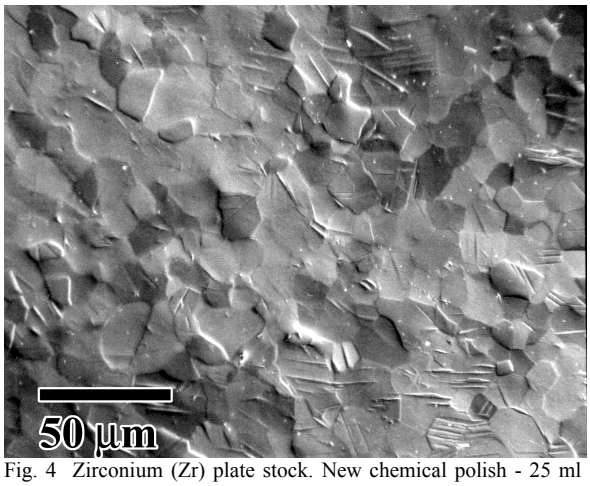

Fig. 4 Zirconium (Zr) plate stock. New chemical polish - 25 ml lactic, 15 ml HNO_3, 5 ml HF swab ~ 5 seconds (tends to bubble – cycle is complete, when bubbles dissipate). (polarized light or DIC) Photographed in DIC.

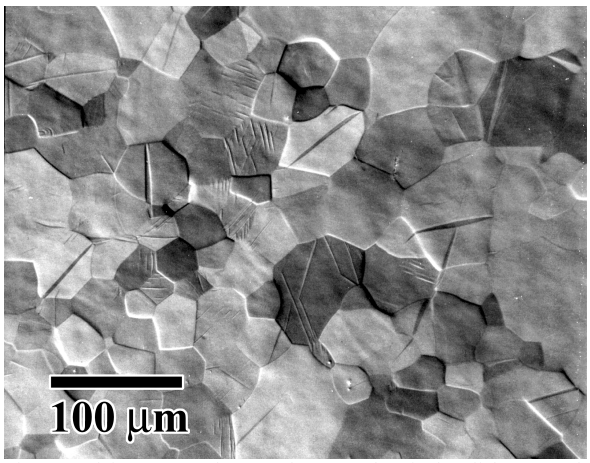

Fig. 6 Hafnium (HF) plate stock. New chemical polish - 25 ml lactic, 15 ml HNO_3, 5 ml HF swab ~ 5 seconds (tends to bubble – cycle is complete, when bubbles dissipate). (polarized light or DIC) Better grain definition, less twinning. Photographed in DIC.

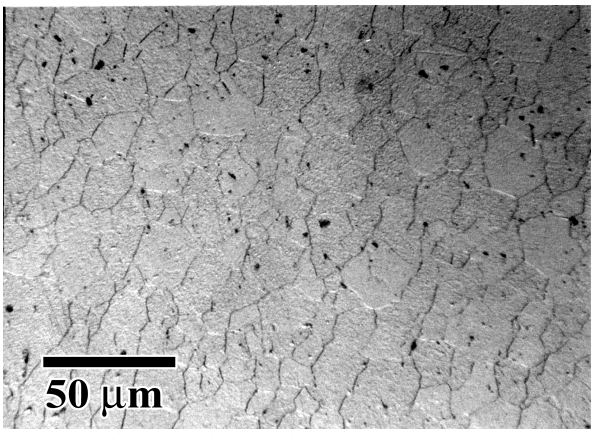

Fig. 7 Vanadium (V) sheet stock. Etchant (ASTM 197), 100 ml H_2O, 5 grams oxalic acid. Electro etch at 6 volts for ~ 5 seconds (bright field or DIC) Photographed in DIC to bring out microstructural detail, sample is etch pitted.

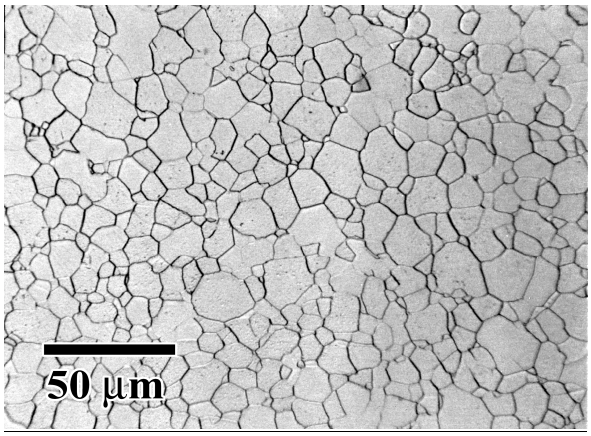

Fig. 8 Vanadium (V) sheet stock- New chemical polish - 25 ml lactic, 15 ml HNO_3, 5 ml HF swab ~ 5 seconds (tends to bubble – cycle is complete, when bubbles dissipate). anodize in a 4% solution of HBF_4 (Barker reagent) @ 15 volts for ~ 2 seconds (light orange color swish through anodizing solution to remove discoloration). Better grain definition, (polarized light or DIC). Photographed in DIC.

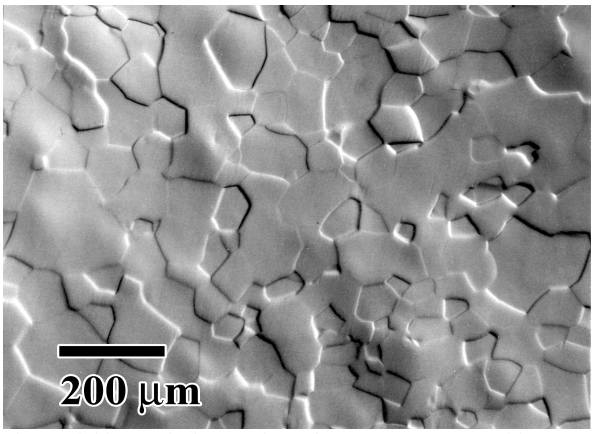

Fig. 9 Niobium (Nb) bar stock. Etchant (ASTM 162a and b.) 162 a. chemical polish: 50 ml lactic acid, 30 ml HNO_3, 1 ml HF swab for ~ 120 seconds. 162 b. niobium etch: 30 ml lactic acid, 10 ml HNO_3, 10 ml HF swab for ~ 20 seconds (photograph in DIC or bright field) Photographed in DIC.

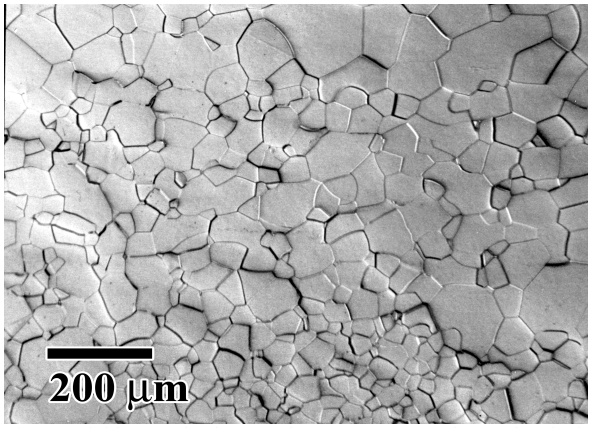

Fig.10 Niobium (Nb) bar stock. New Preparation -Chemical polish =25 ml lactic, 15 ml HNO_3 , 5 ml HF 120 seconds followed by etching with 10 ml HNO_3, 10 ml HF, and 30 ml H_2SO_4) - ~ 30 seconds (photograph in DIC or bright field) better grain definition. Photographed in DIC.

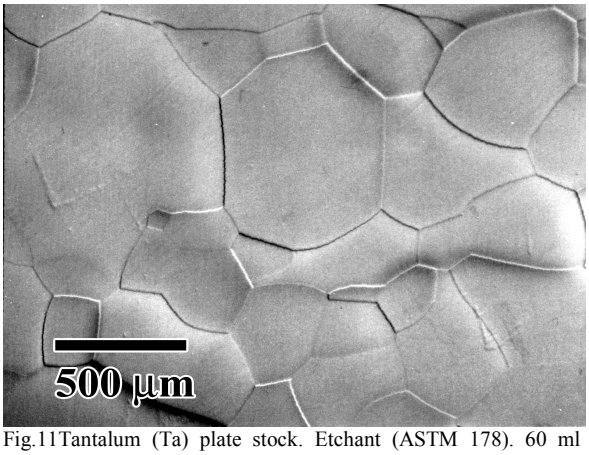

Fig.11Tantalum (Ta) plate stock. Etchant (ASTM 178). 60 ml lactic acid, 20 ml HNO_3, 20 ml HF- swab for ~ 150 seconds (bright field or DIC) Photographed in DIC.

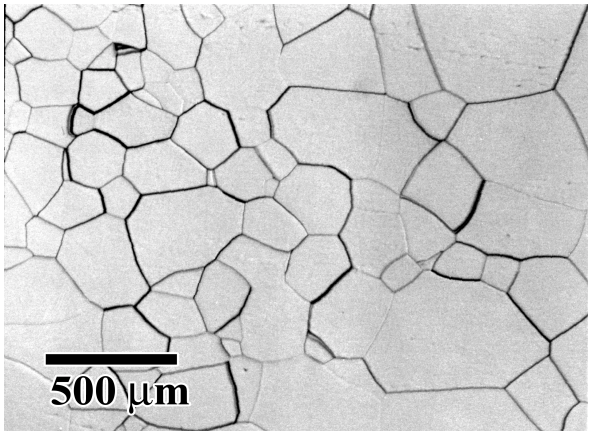

Fig.12 Tantalum (Ta) plate stock. New Preparation - Chemical polish =25 ml lactic, 15 ml HNO_3 , 5 ml HF 120 seconds followed by etching with 10 ml HNO_3, 10 ml HF, and 30 ml H_2SO_4 - ~ 30 seconds) Better grain definition, same results are achieved either with bright field or DIC. Photographed in DIC.

apparent and microstructure is less twinned (photo in DIC). Figures 7 and 8 (vanadium sheet) show a definite improvement in overall microstuctural definition using the new preparation technique. It was necessary to photograph fig. 7 in DIC to bring out the less defined grain structure. Figures 9 and 10 (niobium bar stock) again show that the recommended etchant (Fig. 9) does not produce well defined grain boundaries while Fig. 10 has well defined boundaries (photo in DIC). In figures 11 and 12 (tantalum plate) grain boundaries are unmistakably better defined with the new technique (Fig. 12). (photo in DIC).

4. Conclusions

The goal of this study was to find a process, which would reduce preparation time and provide equal or better results than were obtained by standard metallographic methods. The use of alumina polishing slurry has substantially reduced polishing time. The development of the new chemical polishing technique has universal application to the class IVA and VA materials. The combination chemical polish/etchant or chemical polish/anodizing process produces a high quality microstructural definition in both alloyed and unalloyed material. Finally, the combination chemical polish/etchant eliminates the need for mechanical polishing of tantalum and zirconium if a grain size determination is the only requirement

References

1) A.M. Kelly, S.R. Bingert, R.D. Reiswig, "New Tantalum Metallographic Preparation Techniques for Tantalum and Tantalum Alloys", Microstructural Science, vol.23 (1996) pp. 185-195.
2) A.M.Kelly, S.R. Bingert, Dan J. Thoma, "Application of New Tantalum Metallographic PreparationTechniques to Group IV and V Metals",Microstructural Science, vol. 26 (1998) pp.347-353
3) ASTM E407-93, "Standard Practice for Microetching Metals and Alloys", Annual Book of ASTM Standards, volume 3.01 (1994) pp 438-455.